

cluster and provide avenues for the assignment of residues by site-directed mutagenesis and the refinement of computational and mechanistic models of PSII. This study is supported by the Office of Basic Energy Sciences, United States Department of Energy (DE-FG02-0ER06-15).

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Biochemical and Spectroscopic Analysis of Some Specific Cyanobacterial Species under Some Environmental Stress

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Sensor is a device which is used for the identification and estimation of an analyte. Several researches have shown the development of various types of sensors but an efficient, cost-effective and portable sensor is still required for the easy monitoring of water pollutants. PSII is the membrane protein complex found in oxygenic photosynthetic organisms which harnesses light energy to split H₂O into O₂, protons and electrons. A single celled cyanobacterial species is like chloroplast of higher plants. We have attempted using whole cells and permeabilised spheroplasts as a biosensing material for biosensor designing. We have observed the changes in their UV-Vis spectral properties, peak shifting, spectrofluorometric properties and oxygen evolution properties. The output results were available in a short time span. This property is most useful because its physiological activity can be easily monitored by amperometric/potentiometric systems. Such a biosensor will find application in the assessment of pollutants such as herbicides and heavy metals which affect electron transport in Z scheme of photosynthesis.

Key Words: Biosensor, PS- II particles, Cyanobacteria, Spectral Properties.

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Excitation Dynamics of Light Harvesting Complex 2 B850 Ring

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The dynamics of excitation energy transfer within the B850 ring of light harvesting complex 2 from *Rhodobacter sphaeroides* and between neighboring B850 rings is investigated by means of the hierarchy equations of motion for dissipative quantum mechanics. The assumption of Boltzmann populated donor states for the calculation of inter-complex excitation transfer rates by generalized Förster theory is shown to give accurate results as intra-complex exciton relaxation occurs in about 1 ps. Utilizing generalized Förster theory, the primary channels of exciton transfer between B850 rings are found to be the five lowest-lying exciton states with the non-850 nm states making significant contributions to the total transfer rate.

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Calculation of optical Properties from Molecular-Dynamics Simulations of Light-Harvesting Systems

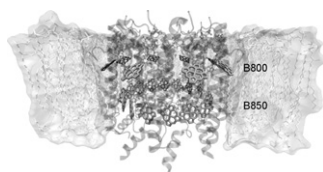
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Harvesting sun light to gain energy for life is initially done by light-harvesting antenna complexes containing chlorophyll and carotenoid molecules. Starting from the available crystal structure of the light-harvesting systems 2 (LH2) of purple bacterium, we applied all-atom classical molecular-dynamics (MD) simulations to the LH2 ring embedded in a membrane. Thus obtained thermal fluctuations of the nuclear positions provide the input for quantum chemical calculations. To obtain the energies of the Q_y excited states of the single Bacteriochlorophyll (BChl) molecules, the semi-empirical ZINDO/CIS method is used to be able to analyze longer time series as was previously possible with the CIS method [1,2]. To include solvent effects to the excited state dynamics, the surrounding atoms of the BChls are treated as classical point charges in the QM calculations. Using the nuclear motion and the obtained energy differences between ground and Q_y excited states with a time-dependent Hamiltonian, we are able to calculate optical properties of the analyzed system.

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Changes in Enthalpy of the Joliot-Kok Four Step Cycle to Produce Oxygen in Photosynthesis

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Changes in Enthalpy of the Joliot-Kok four-step cycle to produce oxygen in photosynthesis.

During photosynthesis, oxygen is produced from water in the four step Joliot-Kok cycle. The kinetics of this cycle have been extensively studied but the thermodynamics are still uncertain. An intriguing possibility is that evolution has found a path that allows a constant free energy difference for all the steps. This would strongly contrast with the sequential one-electron steps where the energies vary by over one electron-volt, or 100 kilojoules. Although the free energy or redox potentials of the intermediates are difficult to assess, the methodology of photoacoustics (PA) allows direct access to the enthalpy of the steps. Essentially the heat or enthalpy liberated by a photo-induced reaction causes an expansion of the media. The resulting sound wave is detected with a microphone. In certain leaves the oxygen itself produces a slower sound wave that can be used to verify the Joliot-Kok cycle of oxygen production. The PA measurement requires a weak pulse of light at the trap wavelength, 680 nm, to determine the enthalpy unalloyed with excess energy, interspersed with saturating pulses to advance the S-states of the Joliot-Kok cycle. A half dozen or more pulse pairs are required to obtain values for the four S-states. To enhance the signal to noise ratio, the cycle is then repeated following several minutes in the dark to allow the system to relax to the known state. The saturating flashes must be spaced by about 300 milliseconds to allow completion of the reaction but not allow decay of the S-states. Very preliminary results indicate that the differences in enthalpies of the reaction steps are small. This work was supported by the Rockefeller University.

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Endor Spectrum of the Protonated Rhodosemiquinone in Bacterial Reaction Centers

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A crucial intermediate state in the reduction of Q_B to Q_BH₂ involves the high energy intermediate Q_BH[•] state. (1) Direct observation of this state was achieved upon replacing the native ubiquinone with the low potential analog rhodosemiquinone (RQ) (2). Here we report the ENDOR spectrum of rhodosemiquinone at low and high pH measured in a mutant RC designed to reduce Q_B via B-branch electron transfer without interference from Q_A^{•-} (3, 4). The peaks at 50.2 MHz and 51.7 MHz (dashed lines) are shifted from the proton Larmor frequency (~53.2 MHz) and are assigned to hydrogen-bonded protons due to their line shape and position and their absence upon exchange in D₂O (4). Upon shift to lower pH, these peaks diminish in amplitude and a new proton peak arises near 49.4 MHz (solid line). We attribute these changes to the protonation of rhodosemiquinone at lower pH. (Supported by NIH)

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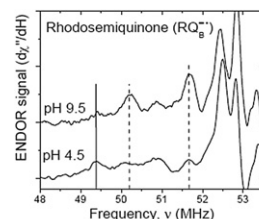


Figure. ENDOR spectrum of rhodosemiquinone in RC at low and high pH ($\nu=35$ GHz, $T=80$ K)

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Novel Photosynthetic Reaction Center Chromophore Configuration

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The *Rhodobacter capsulatus* reaction center mutant M204IQ appears to assemble without the bacteriochlorophyll B_L, which serves as the electron acceptor or mediator of the primary charge separation reaction. Evidence supporting this conclusion to date includes the pigment ratio, low temperature absorption spectrum, steady-state fluorescence and absence of appreciable P⁺Q_A^{•-} formation. If correct, this novel configuration of chromophores will enable many questions about the initial light driven electron transfer in RCs to be probed.

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